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**COMPUTATION OF VIBRATIONAL FREQUENCIES
IN MERCAPTANS, ALCOHOLS, AND SULFIDES**

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<p>We have computed infrared vibrational spectra of a group of halogen-substituted alcohols, mercaptans, and sulfides. The computations are based on the use of the Gaussian 82 Program Package, using Hartree-Fock procedures with the 3-21G basis set. The ultimate goal of the computations is the derivation of theoretical procedures to fill in data gaps in spectral libraries. Predictions are based on a comparison between theoretical and experimental results. In addition, frequency assignments are made by using the computed normal coordinates.</p>					
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PREFACE

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CONTENTS

	Page
1. INTRODUCTION	7
2. COMPUTATIONAL METHODS	8
3. MERCAPTANS	9
4. ALCOHOLS	11
5. SULFIDES	14
6. CONCLUSIONS	18
LITERATURE CITED	19

LIST OF TABLES

Table No.		Page
1	Computed Vibrational Frequencies of Methyl and Ethyl Mercaptans (in Terms of cm^{-1})	10
2	Comparison of Experimental and Computed Frequencies of Methyl and Ethyl Mercaptans (in Terms of cm^{-1})	11
3	Computed Vibrational Frequencies of Methyl and Ethyl Alcohols (in Terms of cm^{-1})	12
4	Comparison of Experimental and Computed Frequencies of Methanol, Ethanol, and 2-Chloroethanol (in Terms of cm^{-1})	13
5	Computed Frequencies of CH_3SCH_3 , $\text{CH}_2\text{ClSCH}_2\text{Cl}$, and $\text{CH}_3\text{SCH}_2\text{Cl}$ (in Terms of cm^{-1})	15
6	Computed Frequencies of $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$ and $\text{CH}_2\text{ClCH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ (in Terms of cm^{-1})	16
7	Comparison of Experimental and Computed Frequencies of CH_3SCH_3 and $\text{CH}_3\text{SCH}_2\text{Cl}$ (in Terms of cm^{-1})	17
8	Comparison of Experimental and Computed Frequencies of Ethyl Sulfide and Chloroethyl Sulfide (in Terms of cm^{-1})	18

COMPUTATION OF VIBRATIONAL FREQUENCIES IN MERCAPTANS, ALCOHOLS, AND SULFIDES

1. INTRODUCTION

In recent years, infrared (IR) spectroscopy has become a favorite method for detecting and identifying unknown atmospheric and environmental substances. We do not intend to discuss the experimental aspects of the detection problem. They have been reviewed in a series of presentations at the 1987 U.S. Army Chemical Research, Development and Engineering Center Scientific Conference on Chemical Defense Research (unpublished data, April 1988). However, we should mention one feature of the experimental approaches. The spectral region between 800 and 1200 cm^{-1} is of particular importance in IR detection methods because this region is most readily accessible to experimental devices.

Detecting known substances whose experimental IR spectra are known is relatively straightforward. However, in many situations, we wish to detect substances of unknown composition or substances of known composition whose experimental IR spectra are not available. In these situations, it would be helpful if the spectra could be predicted by means of theoretical computations. Today, it is possible to predict IR vibrational spectra of medium-sized molecules by using the Gaussian 82 Program Package.¹ The accuracy of the various computational procedures was discussed and results presented in a recent book by Hehre et al.²

Recently, Adams et al. (unpublished data, April 1988) report results of ab initio computations of IR spectra based on the use of the Cambridge Analytical Derivative Package (CADPAC). The goal of these computations is the accurate evaluation of the complete spectra of a group of molecules. We are interested in performing somewhat less accurate computations for a larger group of similar molecules. In a typical case, experimental IR spectra are known for about a third of the molecules in a group that we consider. We hope to predict the IR spectra of all molecules in the group by combining our computational results with the available experimental data. In other words, we hope to fill data gaps in spectral data base sets by using computational results on vibrational IR spectra.

Our present plan involves a study of a group of alcohols, ethers, mercaptans, sulfides, and corresponding fluoro and chloro derivatives. In addition to making numerical predictions, we also hope to derive from our computational results a better understanding of the overall features of the spectra. It is not always possible to accurately predict the whole spectrum of a medium-sized molecule. On the other hand, we find that it is possible to make accurate predictions for

certain specific vibrational modes (e.g., S-H, O-H, C-S, or C-O stretch vibrations, etc.). We find that the frequencies for some of these vibrational modes may be predicted with a much higher degree of accuracy than for others. Therefore, we will focus our attention on those features of the spectra that can be predicted theoretically with the highest accuracy and that are essential for the identification process.

2. COMPUTATIONAL METHODS

Our computations are based on using the Gaussian 82 Program Package. An extensive discussion of the accuracy of the results and possible errors in experimental and computed frequencies may be found in the book by Hehre et al.² We have used those discussions in planning our own work. In preliminary work, we observed that using STO-3G basis sets led to results that are not very accurate, and that using 3-21G basis sets led to results that were considerably more accurate. We also observed that introducing more accurate basis sets did not lead to significant improvement in the accuracy of the computational results. Our observation seems to be consistent with the results and analysis presented by Hehre et al.² Therefore, we decided to base all our frequency computations on using the 3-21G basis set. From similar considerations, we also decided to base our frequency computations on using the straight Hartree-Fock method rather than additional configuration interaction or Moeller-Plesset computations.

Although frequency computations are all based on the harmonic approximation, experimental potential curves may exhibit significant degrees of anharmonicity. For instance, the potential curve of the hydrogen molecule is anharmonic and asymmetric. In this case, the difference between the harmonic and experimental vibrational frequency may be as high as 6%. Also, in the frequency computations, it is assumed that all energy gradients are zero. Hehre et al.² observed that small errors in the molecular geometries can lead to significant errors in the theoretical frequency results. Therefore, we used the option *opt = tight* in all our computations to be sure that we used the correct 3-21G optimized geometries in our frequency computations.

We consider four different groups of organic molecules:

- mercaptans
- alcohols
- sulfides
- ethers

We discuss these four groups separately in the following sections.

We have computed the 3-21G optimized geometries and the vibrational frequencies of the following group of mercaptans: H_3SH , CH_2FSH , CH_2ClSH , $\text{CH}_3\text{CH}_2\text{SH}$, $\text{CH}_2\text{FCH}_2\text{SH}$, $\text{CH}_2\text{ClCH}_2\text{SH}$.

We list a selection of our frequency results in Table 1. The computations produce the detailed forms of the normal coordinates in addition to the frequencies of all normal modes. Therefore, it is possible to assign the different vibrational modes to specific localized motions. We identify various stretch modes corresponding to the C-S, S-H, C-F, and C-Cl bond stretch modes. These assignments seem to be quite obvious, and we list them and their frequencies in Table 1. According to Table 1, these stretch frequencies do not vary significantly from one molecule to another. For instance, it seems reasonable to assume that the S-H stretch motion is not going to be affected much by substitutions at the other end of the molecule. We conclude that the S-H stretch frequencies for the ethyl mercaptans should be very close to each other (agree with Table 1). It should be noted also that the C-Cl stretch frequencies in the methyl and ethyl compounds are practically the same. Again, this seems reasonable. The behavior of the C-C stretch frequencies is less predictable. Here, it should be realized that the two carbon atoms move in conjunction with the attached hydrogens and halogens and that the C-C stretch motion is less localized and less predictable than the other stretch modes. Nevertheless, the C-C bond stretch mode is easily identified from the normal coordinates.

In addition to the bond stretch frequencies, we have identified two different S-H bending modes. It should be noted that the S-H bond is close to being orthogonal to the S-C bond (the bond angle is close to 98°). The H-S-C bending motion occurs in conjunction with a rocking motion of the three hydrogens. The two bending motions may be either in- or out-of-phase. Of course, these assignments become more complicated after substituting a halogen for one of the hydrogens, and the assignments are also less straightforward for the ethyl than for the methyl mercaptans.

Table 1. Computed Vibrational Frequencies of Methyl and Ethyl Mercaptans (in Terms of cm^{-1}).

Mode	CH_3SH	CH_2FSH	CH_2ClSH
C-S stretch	682.1	700.2	739.7
S-H stretch	2626.8	2636.7	2637.3
C-X stretch	-	1168.8	638.1
S-H bend I	849.5	854.8	825.4
S-H bend II	1186.7	1127.0	1063.6
CH_2 wag	1504.7	1490.4	1372.2
H-C-H scissor	1062.7	1364.8	1282.9

Mode	$\text{CH}_3\text{CH}_2\text{SH}$	$\text{CH}_2\text{FCH}_2\text{SH}$	$\text{CH}_2\text{ClCH}_2\text{SH}$
C-S stretch	654.1	666.1	667.0
S-H stretch	2621.0	2614.6	2615.7
C-X stretch	-	1175.6	637.9
C-C stretch	1027.6	1197.8	1121.7
S-H bend I	797.1	836.7	849.0
S-H bend II	948.1	967.9	1041.4
CH_2 wag m	1431.3	1466.0	1437.1
CH_2 wag end	1580.9	1568.7	1635.7
H-C-H scissor	1165.9	1376.2	1288.8

The other vibrational modes involve wagging, rocking, and scissor motions of the CH_2 and CH_3 groups, and the corresponding assignments become more complicated. However, the most intense and important spectral line from our point of view involves a wagging motion of the CH_2 group adjacent to the sulfur. This spectral line is considered to be characteristic of a mercaptan. Therefore, it is necessary to identify the corresponding vibrational mode and frequency. The substitution of a chlorine atom lowers this wagging frequency by about 100 cm^{-1} (Table 1). We have also identified an H-C-H scissor-type bending mode in the terminal CXH_2 group. This frequency is typical for a terminal CClH_2 or CFH_2 group. Finally, we should mention the C-H stretch frequencies. Our computed values are all in a narrow range between 3250 and 3400 cm^{-1} . The values are consistently higher (10%) than the corresponding experimental values. However, the C-H stretch frequencies are of no particular use for identification purposes, and we will not pay any further attention to them.

Experimental information is available only for methyl and ethyl mercaptans. The Raman spectra for both molecules were reported by Wagner.^{3,4} The experimental IR spectrum of methyl

mercaptan was reported by Hehre et al.² The spectrum of ethyl mercaptan may be found in the Aldrich Library of Infrared Spectra.⁵ We present our computed frequencies and both sets of experimental values for methyl and ethyl mercaptans in Table 2. The accuracy of the Aldrich values is about one-half percent. The assignments of the bond stretch frequencies is straightforward, but we are not always completely sure about some of the other assignments, especially if they involve sets of frequencies that are close together. However, we have tried to do the best possible. The most intense spectral line for ethyl mercaptan is at 1269 cm^{-1} , and it involves the CH_2 wagging motion. This should correspond to the 1266 line in the Raman spectrum and to our computed value of 1431 cm^{-1} . We believe that the corresponding spectral line of methyl mercaptan is at 1319 cm^{-1} experimentally because our computed value is 1505 cm^{-1} .

Table 2. Comparison of Experimental and Computed Frequencies of Methyl and Ethyl Mercaptans (in Terms of cm^{-1}).

Mode	CH_3SH			$\text{CH}_3\text{CH}_2\text{SH}$		
	comp	exp ³	exp ²	comp	exp ⁴	exp ⁵
C-S stretch	682.1	702	708	654.1	656	658
S-H stretch	2626.8	2572	2572	2621.0	2569	2551
C-C stretch	-	-	-	1027.6	973	966
S-H bend I	849.5	803	803	797.1	735	732
S-H bend II	1186.7	1055	1074	948.1	866	866
CH_2 wag	1504.7	1319	1319	1431.3	1266	1269
H-C-H scissor	1062.7	-	976	1165.9	1094	1086

Table 2 shows that the agreement between the computed and experimental bond stretch frequencies is reasonable. The differences are 5% for the C-C stretch, 2% for the S-H stretch, and 3% for the C-S stretch. The CH_2 wag frequencies are about 12% less than the computed values. If we had to make pragmatic predictions about the vibrational frequencies of the halogen-substituted mercaptans then we would correct each computed frequency by the same ratio as in the corresponding mercaptan frequency.

4. ALCOHOLS

We have computed the 3-21G optimized geometries and the vibrational frequencies of the analogous alcohols, namely CH_3OH , CH_2FOH , CH_2ClOH , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_2\text{FCH}_2\text{OH}$, and $\text{CH}_2\text{ClCH}_2\text{OH}$. The

results were all obtained by HF computations using the 3-21G basis set. A selected group of computed vibrational frequencies is listed in Table 3.

Table 3. Computed Vibrational Frequencies of Methyl and Ethyl Alcohols (in Terms of cm^{-1}).

Mode	CH_3OH	CH_2FOH	CH_2ClOH
C-O stretch	1090.1	1198.7	1152.3
O-H stretch	3868.0	3876.7	3881.4
C-X stretch	-	1101.0	622.9
O-H bend I	1152.5	1170.2	1152.3
O-H bend II	1479.9	1498.1	1496.6
CH_2 wag	1637.5	1608.1	1666.2
H-C-H scissor	1253.6	1375.3	1283.3

Mode	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_2\text{FCH}_2\text{OH}$	$\text{CH}_2\text{ClCH}_2\text{OH}$
C-O stretch	1110.1	1126.3	1116.0
O-H stretch	3858.2	3873.0	3870.6
C-C stretch	933.3	1099.4	1078.0
C-X stretch	-	1158.4	727.5
O-H bend I	1155.8	1167.5	1220.6
O-H bend II	1495.6	1477.9	1493.2
CH_2 wag end	1571.4	1573.7	1638.1
CH_2 wag m	1536.9	1685.2	1684.0
H-C-H scissor	891.1	895.5	858.2

It is instructive to compare the values listed in Table 3 with the corresponding values of the mercaptans listed in Table 1. It may then be seen that the C-O stretch frequency is around 1100 cm^{-1} , whereas the corresponding C-S stretch frequency is around 650 cm^{-1} . Similarly, the O-H stretch mode occurs around 3870 cm^{-1} , and the S-H stretch mode occurs around 2625 cm^{-1} .

Again, the various bond stretch vibrational modes may be easily identified from an inspection of the normal coordinates, particularly the C-O, O-H, and C-X modes. The C-C mode is not as well defined, but it is still easily identified.

There are two different O-H bending modes. But, in the alcohols, the C-O-H bond angle is about 110° as compared with an S-O-H bond angle of 98° in the mercaptans. We denote the CH_2

wag as a vibrational mode where the hydrogens in a CH_3 , CH_2 , or CH_2X group move in conjunction. In the ethanols, there are two different CH_2 wags, one in the terminal CH_2X group and one in the middle CH_2 group. Finally, we have identified an H-C-H scissor-type mode.

Table 3's results show that the various bond stretch frequencies remain quite similar in all six molecules. The C-O stretch frequency changes by about 100 cm^{-1} upon fluorine substitution and by about 60 cm^{-1} upon chlorine substitution in the methyl alcohols. In the ethyl alcohols, the distance between the halogen and the OH group is larger, and the effect of halogen substitution on the C-O stretch frequency is smaller. The C-O stretch frequency changes by 15 cm^{-1} upon fluorine substitution and by 6 cm^{-1} upon chlorine substitution. It is interesting to note that the computed O-H bending frequencies are quite similar in all molecules.

Experimental spectra are available for methanol, ethanol, and 2-chloroethanol. We present a comparison between the experimental data and our computed values in Table 4. In the case of methanol, both IR and Raman spectra have been reported by various authors. We have selected the IR frequencies reported by Noether⁶ and the Raman frequencies reported by Wagner.³ There is a large difference between the IR and the Raman values for the O-H stretch frequency in methanol. This difference is due to hydrogen bonding because the IR value is measured in the gas phase and the Raman value in the liquid phase. In the case of ethanol, we only list the Raman frequencies reported by Wagner.⁴ The spectrum of 2-chloroethanol is reported in the Aldrich Library of Infrared Spectra.⁵ The experimental frequencies for 2-chloroethanol were derived from reference 5, but their accuracy is no better than 1%.

Table 4. Comparison of Experimental and Computed Frequencies of Methanol, Ethanol, and 2-Chloroethanol (in Terms of cm^{-1}).

Mode	CH ₃ OH			CH ₃ CH ₂ OH		CH ₂ ClCH ₂ OH	
	comp	IR ⁶	Ram ³	comp	Ram ⁴	comp	exp ⁵
C-O stretch	1090	1034	1033	1110	1046	1116	1079
O-H stretch	3868	3683	3375	3858	3390	3871	3389
C-C stretch	-	-	-	933	878	1078	1025
C-Cl stretch	-	-	-	-	-	727	749
O-H bend I	1152	-	1106	1156	1096	1221	1163
O-H bend II	1480	1346	1359	1496	1274	1493	1294

Table 4. Comparison of Experimental and Computed Frequencies of Methanol, Ethanol, and 2-Chloroethanol (in Terms of cm^{-1}) (continued).

Mode	CH ₃ OH			CH ₃ CH ₂ OH		CH ₂ ClCH ₂ OH	
	comp	IR ⁶	Ram ³	comp	Ram ⁴	comp	exp ⁵
CH ₂ wag end	1638	1455	1469	1571	1483	1638	1389
CH ₂ wag m	-	-	-	1537	1452	1684	1429
H-C-H scissor	1254	1209	-	891	878	858	847

We have ignored the C-H stretch frequencies because they are outside the relevant frequency range and because they are of little use for identification purposes.

We cannot guarantee the accuracy of all our spectral assignments, but we feel that the agreement between theory and experiment is satisfactory.

5. SULFIDES

We have computed the vibrational frequencies and the corresponding normal coordinates of five sulfide molecules, namely dimethyl sulfide, chloromethyl methyl sulfide, chloromethyl sulfide, diethyl sulfide, and chloroethyl sulfide.

We have assumed symmetric geometries for dimethyl and dichloromethyl sulfide. In the latter case, we found that the molecular geometry with the lowest energy corresponds to the configuration where for each CH₂Cl group one hydrogen is in the CSC plane with its CH bond pointing away from the other CH₂Cl group. The other hydrogen and chlorine atoms are above and below the CSC plane pointing towards the other CH₂Cl group. The two chlorine atoms are not close; one is above and the other is below the molecular plane.

It is helpful to use the molecular symmetry in interpreting the vibrational spectrum. If we were to disregard interactions between the two halves in each molecule, each vibrational mode would be two-fold degenerate because the same vibrational motion occurs in each half. Due to the interactions between the two halves, each twofold degenerate vibrational mode is split into two different modes with slightly different frequencies. In the customary notation, one mode has A symmetry, and the other mode has B symmetry. Each pair of matching vibrational modes is easily identified by inspecting the normal coordinates.

In Table 5, we present the symmetry analysis of the vibrational modes of methyl sulfide and chloromethyl sulfide. Here and in subsequent discussions, we ignore the C-H bond stretch frequencies because they are of no particular use in identifying the molecules and because they fall outside the relevant frequency range.

Table 5. Computed Frequencies of CH_3SCH_3 , $\text{CH}_2\text{ClSCH}_2\text{Cl}$, and $\text{CH}_3\text{SCH}_2\text{Cl}$ (in Terms of cm^{-1}).

$\text{CH}_2\text{ClSCH}_2\text{Cl}$				
Mode	A	B	Av	$\text{CH}_3\text{SCH}_2\text{Cl}$
C-Cl stretch	643.6	646.2	644.9	634.7
C-S stretch	723.2	749.7	736.4	743.5
C-H bend	967.3	885.7	926.5	908.2
C-H bend	1282.3	1249.0	1265.7	1263.4
C-H bend	1382.6	1354.2	1368.4	1359.3
C-H bend	1588.1	1583.5	1585.8	1590.4

CH_3SCH_3				
Mode	A	B	Av	$\text{CH}_3\text{SCH}_2\text{Cl}$
C-S stretch	664.5	716.5	690.5	674.5
C-H bend	1152.8	1018.5	1065.6	1073.5
C-H bend	1045.5	1075.7	1060.6	1103.4
C-H bend	1515.9	1487.4	1501.6	1504.8
C-H bend	1637.7	1648.2	1642.9	1637.5
C-H bend	1652.5	1643.2	1647.8	1644.4

It is interesting to compare the vibrational frequencies of the three molecules, methyl sulfide, chloromethyl sulfide, and methyl, chloromethyl sulfide. If we take the average of a corresponding pair of A and B frequencies, we should obtain the unperturbed frequency for either the methyl sulfide or the dichloromethyl sulfide molecule. The other molecule, methyl, chloromethyl sulfide is not symmetric, and each vibrational mode should either be localized in the methyl part and correspond to a mode in methyl sulfide, or it should be localized in the chloromethyl part and correspond to a mode in chloromethyl sulfide. Table 5 shows that this type of correspondence between

the frequencies of $\text{CH}_3\text{SCH}_2\text{Cl}$ and either CH_3SCH_3 or $\text{CH}_2\text{ClSCH}_2\text{Cl}$ emerge quite clearly.

A similar analysis of the vibrational frequencies of ethyl sulfide and chloroethyl sulfide is shown in Table 6. In these molecules, it is possible to identify the C-Cl stretch frequencies, C-S stretch frequencies, and C-C-C bond stretch frequencies. It is not easy to differentiate between the many C-H bend frequencies, and we list them all as a group. The only one of them that may be identified individually is a H-C-H scissor-type mode around 850 cm^{-1} . This mode is a cooperative motion occurring in all CH_2 groups.

Table 6. Computed Frequencies of $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$ and $\text{CH}_2\text{ClCH}_2\text{SCH}_2\text{CH}_2\text{Cl}$ (in Terms of cm^{-1}).

	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$			$\text{CH}_2\text{ClCH}_2\text{SCH}_2\text{CH}_2\text{Cl}$		
	A	B	Av	A	B	Av
C-Cl stretch	-	-	-	681.5	702.3	691.9
C-S stretch	696.2	683.7	689.9	795.2	757.2	776.4
C-C stretch	1031.7	1024.2	1027.9	1114.4	1082.6	1098.5
H-C-H scissor	854.1	874.0	864.1	839.7	852.5	846.1
C-H bend	1140.2	1154.1	1147.2	1032.3	1049.9	1041.1
C-H bend	1196.7	1153.0	1174.8	1244.6	1249.5	1247.0
C-H bend	1401.1	1409.0	1405.1	1387.3	1360.3	1373.8
C-H bend	1449.5	1405.6	1427.5	1433.1	1439.5	1436.3
C-H bend	1579.1	1579.0	1579.0	1458.8	1436.2	1447.5
C-H bend	1648.2	1640.2	1644.2	1641.1	1641.1	1641.1
C-H bend	1667.7	1667.5	1667.6	1646.4	1638.6	1642.5
C-H bend	1672.6	1672.1	1672.4	-	-	-

A comparison between experimental and computed frequencies of methyl sulfide and chloromethyl methyl sulfide is shown in Table 7. The spectrum of methyl sulfide was reported by Fonteyne,⁷ and the spectrum of chloromethyl methyl sulfide was obtained from the Aldrich Atlas.⁵ We were unable to find the experimental spectrum of chloromethyl sulfide. Table 7 shows that the agreement between theory and experiment is satisfactory, particularly for the bond-stretch frequencies. The assignment of the C-H bend frequencies is more difficult because there are so many, and some are very close together. Nevertheless, we feel that the assignments in Table 7 are logically consistent. The differences between the computed and experimental frequencies are as high as 200 cm^{-1} in some cases,

but the differences seem to be quite consistent in both molecules.

Table 7. Comparison of Experimental and Computed Frequencies of CH_3SCH_3 and $\text{CH}_3\text{SCH}_2\text{Cl}$ (in Terms of cm^{-1}).

Mode	CH_3SCH_3			$\text{CH}_3\text{SCH}_2\text{Cl}$	
	comp	IR ⁷	R ⁷	comp	IR ⁵
C-Cl stretch	-	-	-	634.7	642
C-S stretch	664.5	685	690	674.5	696
C-S stretch	716.5	706	742	743.5	749
C-H bend	1018.5	-	-	908.2	838
C-H bend	1045.5	1024	1045	1073.5	963
C-H bend	1075.7	1037	-	1103.4	982
C-H bend	1152.8	-	-	1263.4	1156
C-H bend	-	-	-	1359.3	1233
C-H bend	1487.4	1310	-	1504.8	1315
C-H bend	1515.9	1323	1327	1590.4	?
C-H bend	-	1335	-	-	-
C-H bend	1637.7	-	-	1637.5	1402
C-H bend	1643.2	1435	1425	1644.4	1435
C-H bend	1648.2	1445	1443	-	-
C-H bend	1652.5	1459	-	-	-

A similar analysis of the spectra of ethyl sulfide and chloroethyl sulfide is presented in Table 8. The ethyl sulfide spectrum was obtained from the Aldrich Atlas,⁵ and the chloroethyl sulfide spectrum was recently measured by Kroutil (private communication). We identified the various bond-stretch vibrational modes without difficulty and found that the agreement between theory and experiment is satisfactory. In the present case, there are a large number of C-H bending modes; we matched the experimental and computed frequencies by only considering the numerical values. Our matchup seems satisfactory, but we cannot offer any guarantees about its accuracy. In some cases, the differences between the computed and experimental frequencies are as high as 200 cm^{-1} ; it should be noted again that the differences are consistent for all four sulfides considered.

Table 8. Comparison of Experimental and Computed Frequencies of Ethyl Sulfide and Chloroethyl Sulfide (in Terms of cm^{-1}).

Mode	$\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$		$\text{CH}_2\text{ClCH}_2\text{SCH}_2\text{CH}_2\text{Cl}$	
	exp ⁵	comp	exp ⁷	comp
C-Cl stretch	-	-	722	682
C-S stretch	689	696	763	795
H-C-H	778	854	860	840
C-C stretch	970	1032	1038	1114
C-H bend	1046	1140	905	1032
C-H bend	1073	1197	1135	1245
C-H bend	1256	1401	1213	1387
C-H bend	-	1450	-	-
C-H bend	-	-	1300	1433
C-H bend	1370	1579	-	1459
C-H bend	1447	1648	1453	1641
C-H bend	-	1667	-	1646
C-H bend	-	1673	-	-

6. CONCLUSIONS

We feel that our computations and analysis of the vibrational IR spectra of a group of mercaptans, alcohols, and sulfides show that a suitable combination of computational and experimental data presents a convenient procedure for a pragmatic prediction of the vibrational IR spectra of groups of similar molecules.

First, we note that the accuracy of the computed bond stretch frequencies is quite satisfactory with the possible exception of the S-H stretch frequencies. In most cases, the differences between the computed and experimental bond-stretch frequencies are only 10-20 cm^{-1} . Secondly, we feel that the accuracy of the computed frequencies is good enough to make reliable assignments of the various vibrational modes by inspecting the corresponding normal coordinates.

The most important conclusion is that the computational results are of sufficient accuracy and consistency to permit accurate frequency predictions by interpolation and extrapolation for groups of similar molecules. This constitutes a pragmatic and convenient approach to an accurate prediction of IR vibrational spectra of organic and inorganic molecules.

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